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Composition of eroded carbon during its journey through a tropical watershed: a clue to the question whether it is source or sink of CO$_2$

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Abstract

In order to assess whether eroded carbon is a net source or sink of atmospheric CO$_2$, characterisation of the chemical composition and residence time of eroded organic matter (EOM) at the landscape level is needed. This information is crucial to evaluate how fast EOM can be decomposed by soil microbes during its lateral transport. This study considers a continuum of scales to measure the fate of EOM during its transport, across a steep hillslope landscape of the Mekong basin, with intense erosion. Here we show that changes in the chemical composition of EOM (measured by NMR spectroscopy) and in its $^{13}$C and $^{15}$N isotope composition provide consistent evidence for EOM decomposition during the lateral transport of carbon on time scales of less than 50 yr across distances of 10 km. Between individual soil units (1 m$^2$) to a small watershed (10$^7$ m$^2$), the observed 28% decrease of the C/N ratio and the enrichment of $^{13}$C and $^{15}$N isotopes in EOM is of similar magnitude than the enrichment with depth in soil profiles due to soil organic matter “vertical” decomposition. Radiocarbon measurements indicated that these changes are not related to the slow transformation of soil carbon during pedogenesis, but rather to an acceleration of the SOM stabilisation process during its journey through the watershed.

1 Introduction

The decomposition of soil organic matter is one of the most important processes controlling the response of the global carbon cycle to climate and land use change (e.g., Lal et al., 2004). The paradigm of one-dimensional microbial decomposition occurring only at depth in the soil profile, as adopted by all global models, is however highly questionable because of lateral transport of soil organic matter during hydrologic erosion. In this context, it remains controversial whether eroded organic matter (EOM) is a source or a sink of carbon (Van Oost et al., 2007, 2008; Lal and Pimentel, 2008; Kuhn et al., 2009). Organic matter erosion has long been considered to represent a major source
of atmospheric CO$_2$ (Jacinthe and Lal, 2001), but recent modelling evidence suggests that agricultural erosion could lead to a removal of 0.06–0.27 Pg of C from the atmosphere per year (Van Oost et al., 2007; Berthe et al., 2007) because erosion transports otherwise labile carbon into landscape elements where its decomposition is slowed down. Therefore, the lability of EOM needs to be quantified and understood. Recent studies suggest that EOM is not mineralised during the erosion event but rather re-deposited within or exported from the catchment (Wang et al., 2010). There is general consensus that organic matter of the light particulate fraction is subject to preferential detachment and transport by erosion (Gregorich et al., 1998; Rodriguez-Rodriguez et al., 2004). This erodible SOM fraction is usually composed of structurally labile plant litter compounds, such as proteins and polysaccharides, with minor contribution of more recalcitrant structures, such like lignin and cutin (Kölbl and Kögel-Knabner, 2004). As a result the potential carbon mineralisation from eroded sediments is usually enhanced after detachment compared to bulk soil (Jacinthe et al., 2002; Mora et al., 2007; Juarez et al., 2011). The actual mineralisation in the field may however be smaller than often thought, due to formation of dense erosion crusts (Van Hemelryck et al., 2011). Morover, contribution of highly stable organic matter compounds, such as black carbon, found in fire-affected soils under slash and burn agriculture, may remain stable during erosion and transport (Rumpel et al., 2006a).

Ultimately, it is the relative contribution of labile vs. other stable organic matter types to the eroded carbon flux, and their evolution during transport through the landscape, which determines the net C source or sinks balance of EOM.

In this study, we tracked EOM compositional changes of eroded sediments collected at different nested scales in a tropical sub-watershed of the Mekong river, one of the most biochemically active regions of the world because of high erosion rates and tropical climate conditions. Specifically, we measured the elemental, isotopic and bulk chemical composition of sediments eroded from 6 nested scales of observation, going from pedon units of one square meter to the watershed ($10^7$ m$^2$). Data for every scale were recorded during 34 rainfall events of the rainy season of 2003. Depending on the
rainfall intensity SOC transport can be fast during thunderstorms leading to massive soil loss. The aim of the study was to assess the changes occurring in biochemical composition and mean residence time of EOM recovered from different scales (horizontal direction) and to compare them to changes occurring during SOM stabilisation from top- to subsoil horizons (vertical direction).

2 Material and methods

2.1 Study area (geology and climate)

This study was performed in an easily accessible typical sloping land area of northern Laos under traditional slash-and-burn agriculture. The study area is a watershed of 10 km² (i.e., 1 × 10⁷ m²) forming part of the Mekong river basin. It shows high relief formed within silty to sandy shales. Altitudes (Z) range from 280 m at the watershed outlet to 1331 m in the southern part characterized by limestone cliffs. The median Z is 521 m and the coefficient of variation of Z is 78 %. Hill-slopes exhibit steep slopes (average slope gradient of 32 %) and are marked by an asymmetry with short gentle hill-slopes in the northern part and long and steep slopes in the southern part. Alfisols (Soil Survey Staff, 1999) developed from shales are the most common soils in the watershed (Chaplot et al., 2005).

The area is under traditional shifting cultivation and slash and burn agriculture (SBA), where patches of secondary forest and woody/bushy fallows are cleared, the ground residues are burnt to enable cultivation for a short period before the land is allowed to revert to fallow re-growth. Secondary forests cover about 15 % of the whole surface area, mostly on the crest tops.

The climate is marked by a study area has a tropical climate with two distinct seasons. The 30 yr average annual rainfall is 1403 mm and the mean annual temperature is 25 °C. Rainfall exceeds evapo-transpiration throughout the rainy season. The months from November to April are the driest. During the study period in 2003, 34 rainstorms
occurred from 25 May to 2 October with a cumulative rainfall amount of 1044 mm. These events exhibited amounts of between 4 and 127 mm and eight events had a cumulative rainfall over 40 mm.

2.2 Plot establishment

In a tributary of the Mekong river, we selected 6 nested scales from $1 \, m^2$; $2.5 \, m^2$; $0.6 \times 10^4 \, m^2$, $30 \times 10^4 \, m^2$, $60 \times 10^4 \, m^2$ and $1 \times 10^7 \, m^2$ in an attempt to investigate the different erosion mechanisms of the detachment, transport and sedimentation and those involved in the decomposition of the eroded SOC. While both sediment detachment and runoff generation are certainly point phenomena and may be assessed on micro-plots, sedimentation or EOM decomposition is only operative at a certain distance from the “source” (Bloschl and Sivalapan, 1995). Thus the different observation points associated with the various nested scales along the downstream transport of sediments allowed the localization and the quantification of the sedimentation together with an assessment of the potential fate of EOM during its downstream transfer.

At the hill-slope level, twelve enclosed micro-plots of $1 \, m^2$ and eight plots of $2.5 \, m^2$ were installed at 4 positions from the back-slope to the upslope. These micro-plots are part of the micro-catchment of $0.6 \times 10^4 \, m^2$ under the third year of rice production following a 4 yr fallow period. The weir of the $0.6 \times 10^4 \, m^2$ micro-catchment was constructed within the hill-slope, at the back-slope position and collected surface runoff and sediments. It exited in the main Houay Pano flume with a permanent flow to the watershed outlet. In this paper the term “micro-plot” is used for the $1 \, m^2$ areas, and “plot” for the $2.5 \, m^2$. The term “micro-catchment” is used for an area of $0.6 \times 10^4 \, m^2$, “catchment” for both the $30 \times 10^4$ and $64 \times 10^4 \, m^2$ surfaces and “watershed” for the $1 \times 10^7 \, m^2$ surface area.

Field measurements were carried out from May immediately after the sowing of rainfed rice to November following the harvest. The plots were weeded in mid June, late July and at the end of August. Weeding was performed by shallow tilling (0–2 cm) with a hoe.
2.3 Soil sampling for the estimation of SOC content

Soil surface samples (0–5 cm) of the bare soil were collected in twelve 1 m² plots and eight 2.5 m² plots. Three randomly chosen sampling locations were selected in the vicinity of each plot. The samples were collected manually, mixed, air-dried at room temperature, and passed through a 2 mm sieve for further analysis of the soil organic carbon.

2.4 Estimation of runoff, sediment and SOC losses by water erosion

The amount of runoff, sediment and EOM discharged from each of the nested scales was estimated by using buckets for the 1 and 2.5 m² plots and an automatic water level recorder and water sampler that sampled continuously during flooding events at the weirs installed from $0.6 \times 10^4$ to $1 \times 10^7$ m². After each rainfall event, aliquots were collected in the buckets from the 1 and 2.5 m² plots. All the water samples were oven-dried to estimate sediment concentration and sediment discharge. These samples were later analyzed for total OC, and elemental, chemical and isotopic compositions. Since the surface areas studied were not identical, the different fluxes were compared by calculating the amount of eroded C per surface unit rather than by calculating the total amount eroded from the total surface area. Thus, at all scales, erosion values were estimated in g m⁻².

2.5 Elemental and stable isotope analysis of carbon and nitrogen

OC and N contents were determined by the dry combustion method using a CHN auto-analyser (CHN NA 1500, Carlo Erba) coupled to an isotopic ratio mass spectrometer (VG Sira 10) yielding the ratio of stable OC isotopes ($\delta^{13}$C). Stable N isotope ratios ($\delta^{15}$N) were determined with a CHN analyser coupled to an Isochrom III Isotopic mass spectrometer (Micromass-GVI Optima). Results for isotope abundance were reported in per mil (‰) relative to the Pee Dee Belemnite standard (PDB) and
relative to air N$_2$ for $\delta^{13}$C and $\delta^{15}$N, respectively. Analytical precision was $\pm 0.1$ mg g$^{-1}$ for OC and $\pm 0.05$ mg g$^{-1}$ for N content. Analytical precision for isotope measurements was $\pm 0.3\%$.

2.6 $^{14}$C activity measurements

Measurements of $^{14}$C activity were performed to assess the mean residence time of C within the system. The $^{14}$C activity was measured on CO$_2$ obtained by combustion of solid samples at the accelerated mass spectrometer “AMS” facility “Artemis” in Saclay, France.

2.7 Chemical composition

The chemical composition of EOM was analysed by $^{13}$C CPMAS NMR spectroscopy after demineralisation with 10% hydrofluoric acid. This treatment was found not to alter the chemical composition of organic matter as seen by NMR spectroscopy (Rumpel et al., 2006b). The spectra were recorded on a Bruker DSX-200 NMR spectrometer. Cross polarization with magic angle spinning (CPMAS) (Schaefer and Stejskal, 1976) was applied at 6.8 kHz. The $^{13}$C chemical shifts were referenced to tetramethylsilane. A contact time of 1 m was used and the pulse delay was 400 ms. Solid-state $^{13}$C NMR signals were recorded as free induction decay (FID) and Fourier transformed to yield the NMR spectra. The spectra were integrated using the integration routine of the spectrometer. The chemical shift regions 0–45 ppm, 45–110 ppm, 110–140 ppm, 140–160 ppm and 160–220 ppm corresponded to alkyl C, O-alkyl C, C substituted aryl C, O substituted aryl C and carboxylic C, respectively (Wilson, 1987).
3 Results and discussion

The amount of EOM, and its isotopic and chemical composition collected across a continuum of spatial scales across the small watershed suggest changes in the biogeochemical properties during its transport by erosion (Figs. 1 and 2). Firstly, we observed an increase in the carbon content of eroded sediments from 1 to $2.5 \text{ m}^2$ scale, followed by a decrease at larger scales. The $C/N$ ratio of EOM decreased significantly towards larger scales, going from $C/N = 14$ at the $1 \text{ m}^2$ scale down to $C/N = 10$ at the $10^7 \text{ m}^2$ scale. This suggests either preferential removal of C relative to N by microbial decomposition, or enrichment in nitrogen during EOM transport.

The action of microbial decomposition on EOM at larger scales is evidenced by changes in the stable carbon and nitrogen isotopic ratios, which both increase towards larger horizontal scales (Fig. 2), by 4–5‰ for $^{13}$C and 1–2‰ for $^{15}$N respectively. An isotopic enrichment of similar magnitude is usually observed within soil profiles during organic matter decomposition and stabilisation due to “vertical” microbial processing of labile carbon compounds (Rumpel and Kögel-Knabner, 2011). The biggest increase in $^{13}$C and $^{15}$N content of SOC are found at the scale of $30 \times 10^4 \text{ m}^2$. Further, changes in the radiocarbon content of the samples also occur in horizontal direction, i.e. following transport. The $^{14}$C of EOM tends to continue to decrease from 108 to 104 pMC between soil pedon and watershed scale (Table 1). Overall, the $^{14}$C data indicate that EOM is recent (less than 50 yr old).

Chemical composition of EOM was analysed using solid state $^{13}$C nuclear magnetic resonance spectroscopy. This method gives a good overview of the quantitative contribution of alkyl, O-alkyl, aromatic and carboxyl SOM compounds. Data (Fig. 3) show that the dominant signals representing between 31 and 44% of the signal intensity in the spectra of soils and sediments collected throughout the rainy season at the different spatial scales were those of O-alkyl C (45–105 ppm). These signals are most likely to be related to the presence of polysaccharides (Kögel-Knabner, 1997). The peaks between 0–45 ppm correspond to the presence of lipids, cutin, suberin and...
other aliphatic bio-macromolecules, all grouped as alkyl C components. The main signal at 32 ppm corresponds to long-chain methylene structures whereas that at 23 ppm corresponded to short-chain or branched structures synthesized by microorganisms during biodegradation (Baldock et al., 1989; Golchin et al., 1996). Signals between 110–160 ppm corresponded to aryl C, mainly lignin-derived phenols: protonated, C-substituted and O-substituted aromatic C (Knicker et al., 1993). The main signal at 130 ppm represented C-substituted aromatic C, which may be derived from stable aromatic compounds, such as black carbon (e.g. Skjemstad et al., 1996). No distinct signal was found between 130 and 160 ppm, in the spectrum area corresponding to tannins and tannin-like structures.

$^{13}$C CPMAS NMR spectroscopy indicated that at 1 and 2.5 m$^2$ scale, EOM is dominated by an aromatic signal between 110 and 160 ppm most likely related to the presence of fire-derived black carbon, produced during slash-and-burn agriculture (Rumpel et al., 2006b). Towards larger scales this signal is decreasing in favour of O-alkyl C structures, indicators of easily degradable polysaccharide material and alkyl C (Fig. 4). This is illustrated by and increasing O-alkyl/aryl ratio (Table 1). Moreover, the alkyl/O-alkyl ratio is decreasing at greater scales. Consistent with the elemental and stable isotope data, the O-alkyl and alkyl compounds may be microbial-derived.

It is interesting to note, that changes in chemical and stable isotope composition observed during erosion are also occurring with depth in soil profiles (Rumpel et al., 2008). Quantitative evaluation of carbon erosion showed, that only 2% of the initially EOM reaches the outlet of the watershed (Chaplot et al., 2005). Estimates on the carbon remaining in soil following humification and stabilisation processes are in a similar range (Rasse et al., 2006). However, the timescales on which these changes are occurring are quite different in vertical and horizontal direction (> 500 yr in vertical and < 50 yr in horizontal direction). Our data suggest in accordance with other work on OM compounds stabilised by pedogenic processes (e.g. Kiem and Kögel-Knabner, 2003; Spielvogel et al., 2008; Rumpel et al., 2010) that EOM compounds are mainly microbial-derived carbohydrates, which are stabilised due to interaction with the min-
eral phase. Desorption and in turn mineralisation of these labile compounds when reaching fresh and/or saltwater systems is limited (Butman et al., 2007). We conclude that OM stabilisation is greatly accelerated during the erosion process.

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References


Table 1. $^{14}$C activity and ratios of chemical groups as seen by $^{13}$C CPMAS NMR spectroscopy determined for soil and eroded sediments at different scales.

<table>
<thead>
<tr>
<th>Scale</th>
<th>Size ha</th>
<th>$^{14}$C activity pmC</th>
<th>alkyl C/O-alkyl C</th>
<th>O-alkyl C/aryl C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sol</td>
<td></td>
<td>112.1 ± 0.6</td>
<td>0.69</td>
<td>1.14</td>
</tr>
<tr>
<td>Microplot</td>
<td>1 m$^2$</td>
<td>n.d.</td>
<td>0.74</td>
<td>1.03</td>
</tr>
<tr>
<td>Plot</td>
<td>2.5 m$^2$</td>
<td>n.d.</td>
<td>0.71</td>
<td>1.35</td>
</tr>
<tr>
<td>Micro-catchment</td>
<td>0.6 × 10$^4$ m$^2$</td>
<td>108.1 ± 0.6</td>
<td>0.63</td>
<td>2.05</td>
</tr>
<tr>
<td>Catchment</td>
<td>30 × 10$^4$ m$^2$</td>
<td>108.3 ± 0.6</td>
<td>0.57</td>
<td>2.10</td>
</tr>
<tr>
<td></td>
<td>64 × 10$^4$ m$^2$</td>
<td>109.0 ± 0.6</td>
<td>0.56</td>
<td>2.44</td>
</tr>
<tr>
<td>Watershed</td>
<td>1 × 10$^7$ m$^2$</td>
<td>104.5 ± 0.6</td>
<td>0.60</td>
<td>2.69</td>
</tr>
</tbody>
</table>
**Fig. 1.** Boxplot of organic carbon content (A), nitrogen content (B) and C/N ratio (C) for the bulk soil and for sediments collected at the different spatial scales under study. Mean values, standard errors and standard deviations were computed from the different plot repetitions and from the 34 rainfall event under study.
Fig. 2. Boxplot of $d^{13}C$ (A), $d^{15}N$ (B) for the bulk soil and for sediments collected for the soil and at the different spatial scales under study. Mean values, standard errors and standard deviations were computed from the different plot repetitions and from the 34 rainfall event under study.
Fig. 3. Chemical composition of OC in soil and eroded sediments at different scales. Note that at three scales sediments sampled at several dates throughout the rainy season were analysed.
Fig. 4. Proportion of signal intensity of EOM collected at different spatial scales assigned to aryl C, alkyl C and O-alkyl C.